

## Issues in the Field Measurement of VOC Emission Rates

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### ABSTRACT

The measurement of VOC emission rates in the field can be valuable in indoor air quality research, in evaluations of the indoor air quality impacts of design, and in the diagnosis of indoor air quality problems. Current approaches to measuring these emission rates have been based on a single-zone mass balance and have employed a number of simplifying assumptions. This paper reviews the mass balance theory employed in field measurements of VOC emission rates. Some concerns associated with these measurements are discussed including the assumption of equilibrium VOC concentrations and the neglect of adsorption and desorption of VOC on building surfaces. Computer simulations are described that provide an order-of-magnitude assessment of the impacts of these issues.

### INTRODUCTION

A number of situations exist in which it is useful to assess the emission of volatile organic compounds (VOC) in buildings. These include research projects in which one is attempting to understand variations in emission rates over time and as a function of material selection and treatment. Also, when diagnosing the cause of indoor air quality complaints, it is sometimes helpful to understand VOC emissions. Finally, some buildings are designed to have low VOC emission rates, and these emission rates must be measured to determine whether this objective has been realized. A number of approaches are available for assessing VOC emissions in buildings, including the estimation of emission rates. Such estimates are based on a single zone mass balance and measured values of indoor and outdoor VOC concentrations and building air change rates (1-4). However, these estimates of VOC emission rates generally employ a number of simplifying assumptions and do not consider all important mass transport mechanisms. In addition to the estimation of emission rates, the assessment of VOC emissions in buildings can also include the classification of VOC sources based on the ratio of the indoor and outdoor concentrations (5-7). This paper examines the mass balance theory relevant to measuring VOC emission rates and the application of this theory in the field. A number of potential problems with the field measurements of emission rates are identified and discussed, and simulation results are presented that show the potential impacts of these issues.

### THEORY AND MEASUREMENT

Measurement of VOC emission rates in the field have been based on a single zone mass balance applied to a whole building or to a portion of a building (8-9). This mass balance can be expressed as follows:

$$\frac{dC}{dt} = PC_{out}A + \frac{S}{M} - (A + k)C \quad (1)$$

where  $C$  = indoor concentration in mg/kg of air,  $C_{out}$  = outdoor concentration,  $t$  = time in h,  $P$  = penetration factor (dimensionless),  $A$  = air change rate in  $h^{-1}$ ,  $M$  = mass of air in the space in kg,  $S$  = VOC source strength in mg/h, and  $k$  = net rate of indoor removal other than ventilation in  $h^{-1}$ . The penetration factor  $P$  accounts for the loss of VOC when the outdoor airstream enters the building due to filtration effects of leaks in the building envelope and the building ventilation system. The removal term  $k$  accounts for the net impact of irreversible

sinks, that is materials in the building which adsorb VOC from the air and do not release them. It also accounts for VOC adsorption into and subsequent desorption from building surfaces, sometimes referred to as “reversible sinks.” At any given time,  $k$  can be positive or negative, with a positive value corresponding to a net removal of VOC and a negative value corresponding to a net re-emission. Equation (1) is generally used with measured VOC concentrations based on a sampling period of minutes to hours in combination with measured air change rates over the same period. Therefore, one must modify Equation (1) into a form based on an average concentration over a sampling period.

When estimating VOC emission rates in the field,  $C_{out}$ ,  $A$  and  $k$  are generally assumed constant. Equation (1) is then integrated from  $t = 0$  to  $t = T$ , covering the air sampling period,

$$C(T) - C(0) = PAC_{out}T + \frac{1}{M} \int_0^T S \, dt - (A + k) \int_0^T C(t) \, dt \quad (2)$$

Solving Equation (2) for the source term  $S$  yields

$$\int_0^T S \, dt = M [C(T) - C(0)] - MPAC_{out}T + M(A + k) \int_0^T C(t) \, dt \quad (3)$$

Another assumption that is made when using this equation in the field, though not always acknowledged, is that the indoor concentration is at steady-state, i.e.,  $C(T) = C(0)$ . Making this assumption, and substituting overbars for average values, yields

$$\bar{S} = M(A + k)\bar{C} - MPAC_{out} \quad (4)$$

Furthermore, it is generally assumed that  $k$  equals 0 and  $P$  equals 1, yielding the familiar steady-state equation relating indoor emission rates to indoor and outdoor VOC concentrations,

$$\bar{S} = MA(\bar{C} - C_{out}) \quad (5)$$

While this equation is valid when the various assumptions apply, it is often used without acknowledgement of these assumptions or evaluation of their validity. The key assumptions upon which Equation (5) is based are that the indoor VOC concentration is at equilibrium, that the values of  $C_{out}$ ,  $A$ ,  $S$ ,  $k$  and  $P$  are all constant, and that  $k$  and  $P$  are equal to zero and one respectively. The constancy of  $C_{out}$  is valid in many cases, but it should be evaluated through measurements of  $C_{out}$  over time. The air change rate  $A$  may or may not be constant depending on the outdoor weather conditions and the manner in which the ventilation system is controlled. The constancy of  $S$  depends on the characteristics of the VOC sources. The value of  $k$  is a more complex issue. Irreversible sinks, if they exist, will make a positive contribution to  $k$ . The contribution to  $k$  from reversible sinks depends on the material properties of these sinks and the concentration history prior to the sampling period. If the indoor VOC concentrations have been increasing prior to the concentration measurements, then the value of  $k$  will generally be positive as the sinks adsorb VOC. If the concentrations have been decreasing, then  $k$  will be negative due to re-emission. In assuming that  $k$  equals 0, one is in effect assuming that there are no sinks of any kind or that the impact of sinks is negligible compared to the impacts of the source and ventilation terms in Equation (4).

## COMPUTER SIMULATIONS

In order to gain some insight into the impact of these issues on the measurement of VOC emission rates in the field, computer simulations of VOC concentrations were made for a fictitious office building using the multizone airflow and contaminant dispersal model CONTAM (10). The simulations were made for a single-zone representation of an office building, with a floor area of 2000 m<sup>2</sup> and a ceiling height of 3.5 m. The air change rate was

assumed to equal 1400 L/s with the system on, based on 140 occupants and 10 L/s per occupant. With the system off, the air change rate was assumed to be 389 L/s, based on a constant infiltration rate of 0.2 h<sup>-1</sup>. The system was assumed to operate on weekdays from 6 a.m. to 6 p.m. and to be off during the weekend. The simulations calculated the concentration of a non-specific VOC over time in response to changes in the ventilation rate and the VOC source strength. The VOC source strength was divided into three parts, corresponding to the building, the ventilation system and the occupant activities. The source strength due to the building was assumed to have a constant value of 0.5 mg/h-m<sup>2</sup>, corresponding to 1000 mg/h for the whole building. The ventilation system was assumed to emit VOC at a rate of 250 mg/h whenever the system was operating. An additional contribution of 750 mg/h was assumed to exist when the people were in the building, from 9 a.m. to 6 p.m. on weekdays. When the building was occupied, the total VOC source strength was therefore 1 mg/h-m<sup>2</sup>, a value that is typical of what has been observed in the field (11). The outdoor concentration was assumed to have a constant value of 0.083 mg/kg of air (0.1 mg/m<sup>3</sup>).

Some of the simulations accounted for adsorption and desorption from building surfaces using a boundary layer diffusion controlled model with a linear adsorption isotherm (12). This model assumes that diffusion across the boundary layer controls the rate of adsorption and desorption. The model requires a number of parameters, and the simulations used the following values: film mass transfer coefficient of 24  $\mu$ m/s, partition coefficient of 1 kg-air/kg-sorbent and an adsorbent mass of 6 kg/m<sup>2</sup> of sorbent surface. These parameters depend on the airflow in the space, the material properties of the sorbent surface and the chemical properties of the VOC, and the values used in the simulations were based on considerations discussed in (12). The adsorbent surface was assumed to be equal to eight times the floor area of the building, based on a value used for fine particles in telecommunications buildings (9). Additional simulations were performed for other values of the partition coefficient and the floor area multiplier. All the simulations were performed over seven days, starting Monday morning at midnight and ending the following Sunday night at midnight. The initial indoor concentration was selected such that the value at the end of the simulation was within 5% of the initial value.

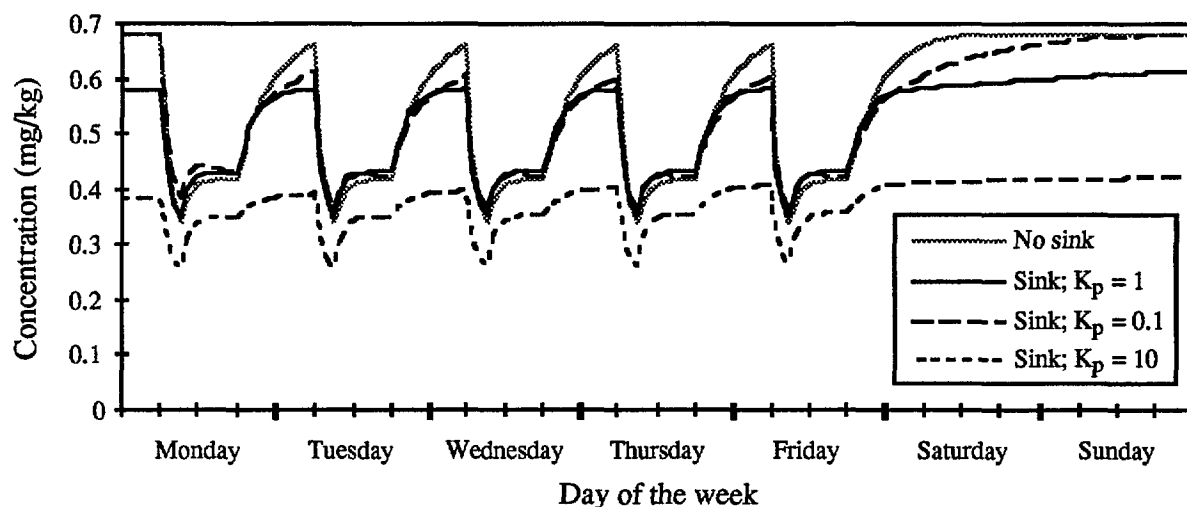


Figure 1 Simulated VOC Concentrations

Figure 1 shows the results of the simulations for four cases. The first case assumes there is no sink, that is the VOC does not react with any interior surfaces and the only loss mechanism is dilution by ventilation air. This case corresponds to the assumptions generally made when measuring emission rates in the field and can be used to assess the impact of using nonequilibrium VOC concentrations to estimate emission rates. The other three cases assume

that the interior surfaces adsorb and desorb VOC and are based on three different values of the partition coefficient  $K_p$ , 0.1, 1 and 10 kg-air/kg-sorbent. The partition coefficient characterizes the capacity of the sorbent surface, with larger values corresponding to the ability to adsorb more VOC. For values of  $K_p$  equal to 0.1 and 1 kg/kg, the impact of the sink is a roughly 10% reduction in the maximum VOC concentration and a smaller increase in the concentration during the day. When  $K_p$  equals 10 kg/kg, the VOC concentration in the air is reduced significantly due to the large sorbent capacity of the surface.

Table 1 Source Strengths Impacts Based on Simulated VOC Concentrations

Sample Time	No sink	$K_p = 0.1$	$K_p = 1$	$K_p = 10$
<b>System-on, occupied</b>				
900-1000	-18%	-9%	-13%	-39%
1000-1100	-9%	-1%	-3%	-28%
1100-1200	-4%	2%	1%	-23%
1200-1300	-2%	3%	3%	-21%
1300-1400	-1%	3%	4%	-21%
1400-1500	0%	3%	4%	-20%
1500-1600	0%	3%	4%	-20%
Average from 900 to 1700	-5%	0%	0%	-25%
<b>System-off, unoccupied</b>				
1800-1900	-40%	-40%	-38%	-54%
1900-2000	-33%	-33%	-32%	-52%
2000-2100	-27%	-29%	-27%	-51%
2100-2200	-22%	-25%	-24%	-50%
2200-2300	-18%	-23%	-22%	-49%
2300-2400	-15%	-21%	-20%	-49%
000-100	-12%	-18%	-19%	-49%
100-200	-10%	-16%	-19%	-49%
200-300	-8%	-15%	-18%	-49%
300-400	-7%	-14%	-18%	-49%
400-500	-5%	-13%	-17%	-49%
500-600	-4%	-12%	-17%	-49%
<b>System-on, unoccupied</b>				
600-700	133%	117%	104%	29%
700-800	66%	65%	55%	1%
800-900	33%	42%	34%	-11%

These simulations can be used to examine the impact of two factors on the estimation of emission rates when using Equation (5), the concentration not being at equilibrium and the lack of an adsorption term. Table 1 shows the percentage difference between the emission rate calculated with Equation (5) and the assumed emission rate for several different sampling periods on the second day of the simulation period. The no-sink case is impacted only by the assumption that the VOC concentration is at equilibrium. Based on the average concentrations over one hour, the source strength is underestimated by about 15% early in the occupied portion of the day. The error diminishes to zero later in the day when the concentration attains its equilibrium value. Based on an average concentration from 9 a.m. to 5 p.m., the source strength is underestimated by 5%. The emission rates when the building is no longer occupied are underestimated early in the evening by 40%, with the degree of underestimation decreasing

to less than 5% as the concentration builds up to its new equilibrium level in the early morning. When the ventilation system comes on in the morning, before the people arrive, the emission rate is significantly overestimated because of the time it takes for the concentration to decrease from its elevated level. These percentages will vary as a function of the ventilation rate, with lower ventilation rates leading to more significant "errors."

The impact of adsorption and desorption on the estimated source strengths is seen in the last three columns of Table 1. For  $K_p = 0.1$  kg-air/kg-sorbent, the estimated source strengths based on one-hour average concentrations when the building is occupied are within 10% of the actual assumed value, and there is no error in the rate based the 8-hour average concentration. These estimates are more "accurate" than the no-sink case because re-emission from the sorbent surfaces increase the VOC concentration in the indoor air during the day as VOC is re-emitted from the sorbent surfaces into the air. This VOC release reduced the impact of using nonequilibrium concentrations early in the day, and leads to only a small overestimation later in the day. However, there are significant errors in the estimated emission rates during the unoccupied portions of the day. Increasing the partition coefficient from a value of 0.1 to a value of 1 increases the impact of the sorbent surfaces to a small degree. The highest value of  $K_p$  has the most significant impact on the estimated source strengths. In this case, the large sorbent capacity decreases the VOC concentration in the indoor air well below the other cases, and results in significant underestimation of the source strength except during the pre-occupancy period of ventilation.

Additional simulations were performed using different values of the floor area factor, that is the ratio of sorbent surface area to floor area. A value of 8 was used in the simulations presented in Figure 1. Simulations were also performed for values of 0.8 and 80. When the floor area multiplier equals 0.8, the sorbent mass is so small that the results are very similar to the no-sink case. When the floor area multiplier is 80, the large sorbent mass decreases the VOC concentrations in the air, leading to estimated sources strengths equal to about one-half of the actual assumed value during the occupied portions of the day.

In addition to the partition coefficient and the floor area multiplier, other factors that will impact the simulation results are the VOC source strength and its variation over time, the air change rate and its variation, the film mass transfer coefficient at the sorbent surface, and the sorbent mass per unit area of sorbent surface. Also, these simulations did not examine the impact of irreversible sinks or values of the penetration factor other than one. The literature contains few values of the relevant parameters, and therefore the estimates of errors in emission rate measurements presented here are clearly preliminary and approximate.

These simulations, by considering transient effects and adsorption and desorption at surfaces, indicate that the ventilation and source profile prior to an emission rate estimate are critical to the accuracy of that estimate. Specifically, emission rate measurements may not be advisable early in the day in buildings where the occupant activities are a significant source of emissions. Also, attempts to measure and compare emission rates under different conditions of occupancy and system operation may be difficult. These results point to the need for additional research to determine more precise values of the parameters discussed here, as well as more study of how the mechanisms that these parameters characterize impact emission rate measurement.

## CONCLUSIONS

The measurement of VOC emission rates in the field has employed a single-zone mass balance approach in conjunction with a number of simplifying assumptions. These assumptions are that the VOC concentration is at equilibrium, there is no loss of indoor VOC other than through dilution by ventilation air, and that there is no loss of outdoor VOC when they enter the

building. The order-of-magnitude computer simulations presented in this paper demonstrate that these assumptions could lead to errors on the order of 25% during occupied periods and as large as 100% under other conditions. Given the uncertainty associated with the inputs to these simulations, it is conceivable that the actual errors in the field could be larger. The equilibrium issue can be dealt with through time-series monitoring to verify that the concentration is at steady state. However, the impact of other assumptions, particularly those regarding loss mechanisms, will require more research.

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